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A novel synthesis of fluorine-containing cyclopentenones *via* Pauson–Khand reaction

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ABSTRACT

Intermolecular Pauson–Khand reaction of fluoroalkylated alkynes with 2-norbornene or 2,5-norbornadiene at the reflux temperature of dichloroethane proceeded smoothly to give the corresponding cyclopentenone derivatives in high yields as a mixture of regioisomers. On the other hand, *intramolecular* Pauson–Khand reaction of fluorine-containing 1,6-enyne proceeded in the presence of NMO or TMANO to give the bicyclic adducts in good yields. Additionally, allyl CF_3-propargyl ether also underwent a smooth Pauson–Khand reaction in the presence of amine oxide, the corresponding bicyclic compounds being obtained in a highly diastereoselective manner.

1. Introduction

2-Cyclopentenone derivatives occupy a central position in organic synthesis owing to their wide utility as potent synthetic blocks, particularly as Michael acceptors for conjugate addition reactions, dienophiles and dipolarophiles for cycloaddition reactions, and so on [1]. 2-Fluoroalkyl-2-cyclopentenones **1**, shown in Fig. 1, are likewise of great synthetic value as building blocks for constructing various types of fluorine-containing compounds, which attract much attention in biological and materials chemistry. Therefore, it is a very significant subject to develop a convenient and effective route to such fluorinated cyclopentenones and related compounds. Nevertheless, there have been quite limited studies on the preparation of 2-fluoroalkyl-2-cyclopentenone derivatives thus far [2]. Herein is disclosed a convenient synthetic approach to **1** *via* Pauson–Khand reaction [3] by using fluoroalkylated alkynes in detail [4].

2. Results and discussion

2.1. Intermolecular Pauson–Khand reaction

Our initial studies focused on the *intermolecular* Pauson–Khand reaction of trifluoromethylated internal alkyne **2a** (Rf = CF_3, R = *p*-ClC_6H_4) [5] and 2-norbornene as shown in Scheme 1 and Table 1. Thus, treatment of **2a** with 1.2 equiv. of $Co_2(CO)_8$ in dichloroethane at room temperature for 2 h gave the corresponding alkyne–cobalt complex **3a** in quantitative yield. Without isolation, 3.0 equiv. of 2-norbornene was added into the reaction mixture, and then the whole was stirred at room temperature for 6 h. However, no desired product was obtained and the alkyne–cobalt complex was recovered almost quantitatively (Entry 1). On the other hand, the reaction at the reflux temperature gave the corresponding adducts in excellent yield (Entry 2). In this case the product was obtained as a diastereomeric mixture in a ratio of 68:32 of **4a** and **5a** [6]. Addition of 1,4-dioxane or MeSPh did not lead to a significant influence on the reaction at all (Entries 3 and 4). In sharp contrast, amine oxide, which is recognized as a very effective promoter for Pauson–Khand reaction in the non-fluorinated system [7], led to a significant decrease of the yield (Entry 5). Several attempts to improve the yield in the amine oxide-promoted Pauson–Khand reaction were fruitless as shown in Entries 6 and 7.

We next examined the Pauson–Khand reaction of various trifluoromethylated internal alkynes under the reflux conditions without a promoter. The results are summarized in Table 2.

As shown in Entries 1–3, the alkynes having an electron-withdrawing or an electron-donating group on the benzene ring were found to be good substrates, the corresponding cyclopentenones **4** and **5** being obtained in high yields as a diastereomeric mixture in a ratio of *ca.* 70:30. The position of the substituent on the benzene ring slightly influenced on the yield (Entries 3–5). Additionally, the opposite regioselectivity was observed in the case of the alkyne **2e** having an *ortho*-substituted aryl group as R (Entry 5). Use of an alkyl substituent and an ethoxycarbonyl group as R caused a significant improvement of the regioselectivity, **4f** and **4g** being obtained preferentially (Entries 6 and 7). When the

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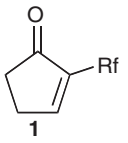


Fig. 1. 2-Fluoroalkyl-2-cyclopentenones.

Table 1
Investigation of the reaction conditions (**a**: Rf = CF_3, R = *p*-ClC_6H_4).

Entry	Promoter	Yield[a]/% of **4a** + **5a**	Isomer ratio[a] (**4a**:**5a**)	Recovery[a]/% of **3a**	Recovery[a]/% of **2a**
1[b]	None	0	–	92	0
2	None	(92)	68:32	4	0
3	1,4-Dioxane	99	73:27	Trace	0
4	MeSPh	94	78:22	0	0
5	NMO	50	69:31	0	0
6[c]	NMO	59	71:29	12	0
7[b]	NMO	12	88:12	32	13

[a] Determined by ^{19}F NMR. Value in parentheses is of isolated yield.
[b] Carried out at room temperature.
[c] Refluxed for 2 h.

difluoromethylated alkyne **2i** was used, the reaction took place very smoothly to afford the corresponding **5i** preferentially, like the reaction of **2e** (*vide infra*) (Entry 9).

We also investigated the Pauson–Khand reaction using various non-fluorinated alkenes. Although the reaction with 2,5-norbornadiene afforded the corresponding cyclopentenone **4j** and **5j** in good yield (Scheme 2), the other alkenes, such as cyclohexene, maleic anhydride, ethylene carbonate, and 1-octene, did not give any trace of the desired products at all.

2.2. Regioselectivity

The regiochemical assignment was carried out based on the ^{13}C NMR chemical shifts of the signals having the coupling constants ^2J(C, F) or ^3J(C, F). In general, it has been recognized in CF_3-containing materials that the coupling constant ^2J(C, F) is *ca.* 30–40 Hz, while ^3J(C, F) is *ca.* 3–5 Hz. The chemical shifts as well as the coupling constants of the Pauson–Khand reaction products **4a**–**g**, **5a** and **b** are collected in Table 3. In the compound **4**, the signal having a larger coupling constant ^2J(C, F) appears at the upper field than the signal having a smaller coupling constant ^3J(C, F). The opposite situation can be observed in **5**. Additionally, it has been

Table 2
Intermolecular Pauson–Khand reaction of various alkynes with 2-norbornene.

Entry	Rf	R	Yield[a]/% of **4** + **5**	Isomer ratio[b] (**4**:**5**)
1	CF_3	*p*-ClC_6H_4 (**a**)	92	68:32
2	CF_3	*p*-$EtO_2CC_6H_4$ (**b**)	91	73:27
3	CF_3	*p*-$MeOC_6H_4$ (**c**)	90	71:29
4	CF_3	*m*-$MeOC_6H_4$ (**d**)	86	69:31
5	CF_3	*o*-$MeOC_6H_4$ (**e**)	(72)[c]	22:78
6	CF_3	*p*-$MeOC_6H_4CH_2$ (**f**)	57	93:7
7	CF_3	EtO_2C (**g**)	69	100:0
8	CF_3	$PhMe_2Si$ (**h**)	0	–
9	CHF_2	*p*-$MeOC_6H_4$ (**i**)	77	31:69

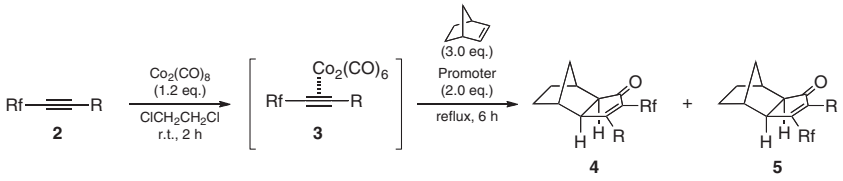
[a] Isolated yield. Value in parentheses is the yield determined by ^{19}F NMR.
[b] Determined by ^{19}F NMR.
[c] The product could not be completely purified because of impurities.

reported that the ^{13}C NMR signal of α-carbon attached with a CF_3 group in the known compound **6** appears at the upper field than that of β-carbon having *ca.* 3 Hz as a coupling constant, though ^2J(C, F) has not been described in the literature [2d]. Consequently, the structure of **4** was determined to be the *exo*-adduct having a CF_3 group at 2 position, while **5** was determined to be the *exo*-adduct having a CF_3 group at 3 position [6].

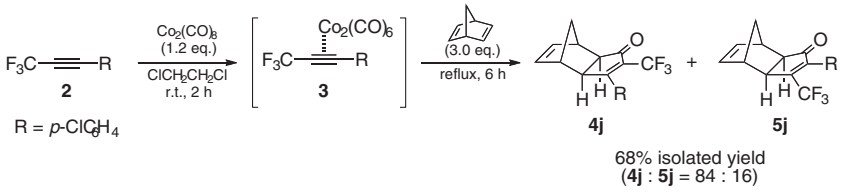
2.3. Reaction mechanism

It has been well recognized that the regiochemistry could be significantly influenced by steric as well as electronic effect in Pauson–Khand reaction of internal alkynes, which leads to a difficult prediction of the regioselectivity. Generally, the bulkier group on the alkynes tends to be located at α position to the carbonyl group. When the substituents on the alkynes are sterically similar, the more strongly electron-withdrawing group tends to be located at the β position to the carbonyl group (Scheme 3) [2d,8].

In the present study, the steric factor, not the electronic factor, might play an important role in the regioselectivity. Thus, a CF_3 group, which is considered to be similar to an isopropyl group in size [9], might be bulkier than a phenyl as well as an alkyl functionality, resulted in a preferential formation of **4**. On the other hand, an *ortho*-substituted aryl group is much bulkier than a *meta*- and a *para*-substituted ones, and maybe a CF_3 group, leading to a preferential formation of **5**. Additionally, a CHF_2 group might be a smaller substituent, compared to an aryl group as well as a CF_3



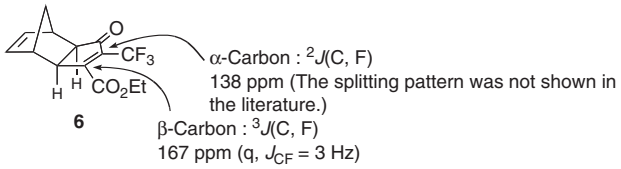
Scheme 1. Intermoleclar Pauson–Khand reaction.

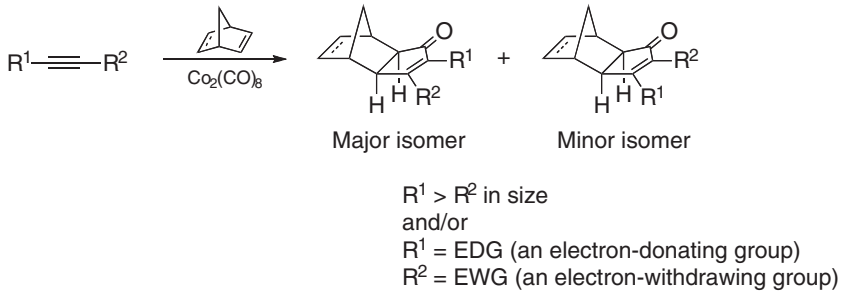


Scheme 2. Intermolecular Pauson–Khand reaction with 2,5-norbornadiene.

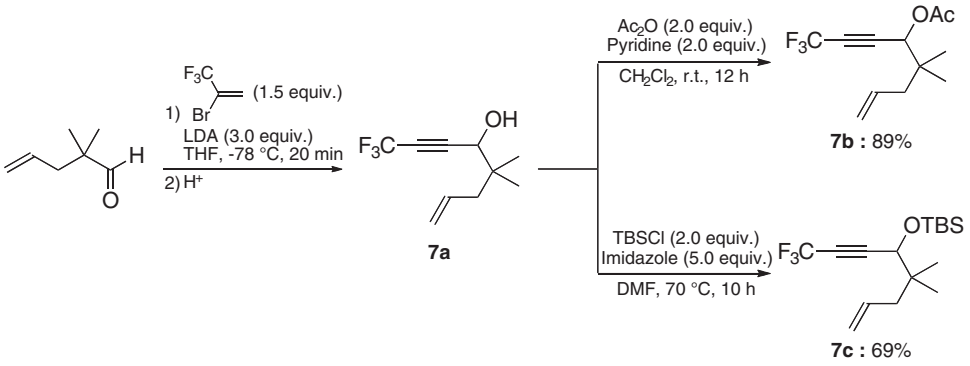
Table 3
The chemical shifts of the signals having ^2J(C, F) or ^3J(C, F) in ^{13}C NMR of **4** and **5**.

	4		**5**	
	α-Carbon: ^2J(C, F)	β-Carbon: ^3J(C, F)	α-Carbon: ^2J(C, F)	β-Carbon: ^3J(C, F)
a	133 (q, J = 31 Hz)	177 (q, J = 3 Hz)	148 (q, J = 3 Hz)	155 (q, J = 32 Hz)
b	134 (q, J = 31 Hz)	178 (q, J = 3 Hz)	148 (q, J = 3 Hz)	156 (q, J = 32 Hz)
c	131 (q, J = 31 Hz)	178 (q, J = 3 Hz)		
d	133 (q, J = 31 Hz)	179 (q, J = 3 Hz)		
f	133 (q, J = 31 Hz)	182 (q, J = 2 Hz)		
g	134 (q, J = 33 Hz)	167 (q, J = 3 Hz)		





Scheme 3. Regioselectivity.



Scheme 4. Preparation of various trifluoromethylated enynes.

group [10], therefore the β-difluoromethylated cyclopentenone derivative **5** being obtained preferentially.

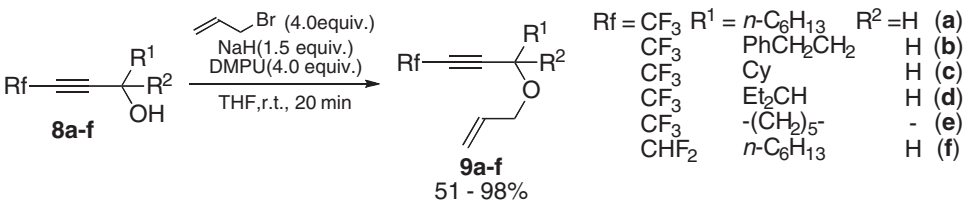
2.4. Intramolecular Pauson–Khand reaction

Our attention was next directed toward the *intramolecular* Pauson–Khand reaction using fluorine-containing 1,6-enynes or ally propargyl ethers.

Various substrates could be prepared according to the conventional method as shown in Schemes 4 and 5. Thus, the nucleophilic addition of trifluoromethylated acetylide with 2,2-dimethyl-4-pentenal afforded 1,1,1-trifluoro-5,5-dimethyl-7-octen-2-yn-4-ol (**7a**) in a good yield [11]. The alcohol could be easily converted into the corresponding acetate **7b** and the silyl ether **7c**.

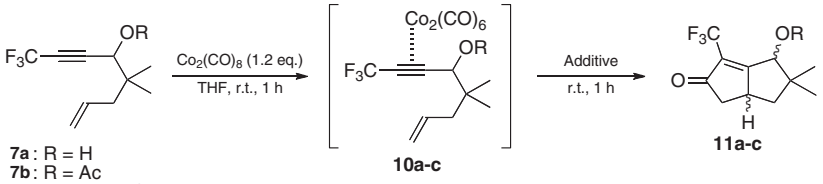
On the other hand, the alcohols **8a**–**f**, prepared readily from 2-bromo-3,3,3-trifloropropene and the corresponding aldehydes, were subjected to 4.0 equiv. of allyl bromide in the presence of 1.5 equiv. of NaH and 4.0 equiv. of DMPU in THF at room temperature for 20 min, the corresponding propargyl ethers being obtained in good to high yields (Scheme 5).

With these substrates, we next examined the *intramolecular* Pauson–Khand reaction in detail (Table 4). Thus, treatment of **7a** with 1.2 equiv. of $Co_2(CO)_8$ in dichloroethane at room temperature for 1 h gave the corresponding alkyne–cobalt complex, **10a**. Without isolation, the complex was allowed to heat at the reflux temperature for 6 h. In sharp contrast to the *intermolecular* Pauson–Khand reaction, the desired [2+2+1] cyclization product was obtained in only 14% yield, and neither the starting material nor the alkyne–cobalt complex were observed (Entry 1). When the reaction mixture was stirred for only 1 h, the desired bicyclic compounds **11a** was obtained in 43% yield as a diastereomeric mixture in a ratio of *ca.* 1:1. In this case, however, any trace of starting alcohol as well as alkyne–cobalt complex was not detected at all (Entry 2). The reaction at room temperature led to 80% recovery of the alkyne–cobalt complex (Entry 3).



Scheme 5. Preparation of various fluorinated propargyl ethers.

Table 4
Intramolecular Pauson–Khand reaction of various enynes



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Entry	R	Additive (equiv.)	Yield[a,b]/ % of **11**	Isomer ratio[a]	Recovery[a]/ % of **10**	Recovery[a] % of **7**
1[c,d]	H (**a**)	None	14	33:67	0	0
2[c,e]	H (**a**)	None	43	44:56	0	0
3[f]	H (**a**)	None	0	–	80	0
4	H (**a**)	None	5	57:43	76	0
5	H (**a**)	NMO (1.5)	58	44:56	3	0
6	H (**a**)	NMO (3.0)	60	58:42	0	0
7	H (**a**)	TMANO (1.5)	39	54:46	27	0
8	H (**a**)	TMANO (3.0)	69 (67)	61:39	0	0
9	Ac (**b**)	NMO (1.5)	41	44:56	11	0
10	Ac (**b**)	NMO (3.0)	37	36:64	0	0
11	Ac (**b**)	TMANO (1.5)	54 (52)	46:54	10	0
12	Ac (**b**)	TMANO (3.0)	44	38:62	3	0
13	TBDMS (**c**)	NMO (3.0)	35	23:77	0	48
14	TBDMS (**c**)	NMO (6.0)	9	0:100	0	44
15	TBDMS (**c**)	TMANO (3.0)	47	37:63	0	38
16	TBDMS (**c**)	TMANO (6.0)	56 (53)	41:59	0	44

[a] Determined by ^{19}F NMR.
[b] Values in parentheses are of isolated yield.
[c] Carried out with 1.2 equiv. of $Co_2(CO)_8$ in $ClCH_2CH_2Cl$.
[d] The reaction mixture of **10a** was refluxed for 6 h.
[e] The reaction mixture of **10a** was refluxed for 1 h.
[f] Carried out in $ClCH_2CH_2Cl$.

Then, we next investigated the promoter as shown in Entries 4–8. Thus, on treating **7a** with $Co_2(CO)_8$ in THF at room temperature for 1 h, the corresponding alkyne–cobalt complex **10a** was afforded, similar to the reaction in dichloroethane. Without isolation, the complex was exposed to 1.5 equiv. of *N*-methylmorpholine-*N*-oxde (NMO) at room temperature for 1 h, giving the corresponding bicyclic compounds, **11a** in 58% yield in a stereorandam manner (Entry 5), while only a trace amount of the Pauson–Khand product was detected in the absence of NMO (Entry 4). Increase of the amount of NMO did not lead to a dramatic improvement of the yield (Entry 6), however, the reaction in the presence of 3.0 equiv. of trimethylamine-*N*-oxide (TMANO) gave the better result rather than the reaction in the presence of 1.5 equiv. of TMANO (Entries 7 and 8).

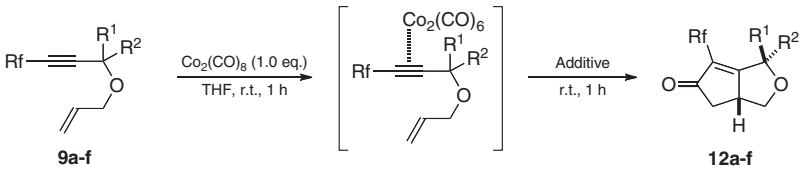
As shown in Entries 9–16, we also examined the *intramolecular* Pauson–Khand reaction using **7b** and **7c**. After several attempts, the acetate **7b** afforded the desired CF_3-cyclopentenone derivative **11b** in 54% yield when the reaction was performed in the presence of 1.5 equiv. of TMANO, while the reaction with **7c** required much more amount of TMANO to produce **11c** in 56% yield. In all cases, the products were obtained as an almost 1: 1 diastereomeric mixture.

Very interestingly, the Pauson–Khand reaction of fluorinated propargyl ally ether **9a** in the presence of TMANO took place relatively smoothly to give the corresponding bicyclic adduct **12a** in a highly diastereoselective manner (Table 5, Entry 1). In this case, only the corresponding *cis* adduct was detected, and no *trans* isomer could not be obtained at all. The similar diastereoselectivity could be observed in the other fluorinated allyl propargyl ether **9b**–**d**, the corresponding bicyclic products being afforded in a highly *cis*-selective manner. However, **9e** was found to be less reactive in Pauson–Khand reaction (Entry 5). In addition, changing a fluoroalkyl group from a CF_3 group to a CHF_2 group caused a significant influence on the reaction, and no product was given at all (Entry 6).

2.5. Stereochemistry

The stereochemical assignment of **12** was determined based on the NOE experiment of **12a**. Thus, a NOE between Ha at δ 3.3 and

Table 5
Intramolecular Pauson–Khand reaction of allyl propargyl ethers



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Entry	Rf	R^1	R^2	Additive (equiv.)	Yield[a,b]/% of **12**
1	CF_3	*n*-Hex (**a**)	H	TMANO (3.0)	(50)
2	CF_3	$PhCH_2CH_2$ (**b**)	H	NMO (1.5)	46 (45)
3	CF_3	*c*-Hex (**c**)	H	NMO (1.5)	46 (35)
4	CF_3	Et_2CH (**d**)	H	NMO (3.0)	57 (51)
5	CF_3	$-(CH_2)_5-$ (**e**)		NMO (1.5)	28
6	CHF_2	*n*-Hex (**f**)	H	NMO (1.5)	0

[a] Determined by ^{19}F NMR.
[b] Values in parentheses are of isolated yield.

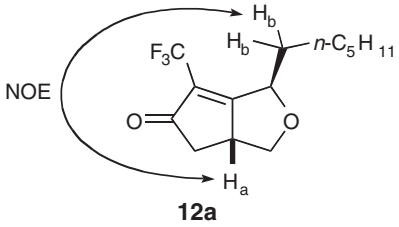

Fig. 2. NOE experiment of **12a**.

Hb at δ 1.7 in **12a** in the NOESY experiment was observed, indicating that Ha and *n*-C_6H_{13} group is in the *cis* configuration relationship (Fig. 2).

3. Conclusion

In summary, we have demonstrated the *intermolecular* as well as *intramolecular* Pauson–Khand reaction by using a variety of fluorinated alkynes. The reaction of the alkynes with 2-norbornene and 2,5-norbornadiene in the presence of a stoichiometric amount of $Co_2(CO)_8$ at the reflux temperature of dichloroethane took place very smoothly to give the corresponding *exo*-adducts in high yields.

On the other hand, fluorinated 1,6-enynes as well as allyl propargyl ethers underwent a smooth Pauson–Khand reaction under the influence of amine oxide, like NMO or TMANO, affording the bicyclic compounds in good yields. It was noteworthy that Pauson–Khand reaction by using propargyl allyl ethers gave the adducts in a highly *cis*-selective manner, while 1,6-enynes afforded the bicyclic compounds in a stereorandam manner.

4. Experimental

4.1. General experimental procedures

Infrared spectra (IR) were recorded on a Shimadzu FTIR-8200A (PC) spectrophotometer and Thermo Electron Corp AVATAR 370DTGS spectrophotometer. ^1H NMR (500.13 MHz) and ^{13}C NMR (125.75 MHz) spectra were measured with a Bruker DRX500 spectrometer or a JEOL JNM-AL400 spectrometer in a chloroform-*d* ($CDCl_3$) solution with tetramethylsilane (TMS) as an internal reference. ^{19}F NMR spectra were measured with a Bruker DPX300 (282.38 MHz) spectrometer or a JEOL JNM-AL400 spectrometer (376.05 MHz) in a $CDCl_3$ solution containing $CFCl_3$ as an internal reference. A JEOL JNM-EX90A (84.21 MHz, FT) spectrometer was used for determining the yields of the products with internal hexafluorobenzene (C_6F_6), trifluoromethylbenzene (BTF), or ethyl trifluoroacetate (TFA). It was also used for the determining regioselectivity and stereoselectivity. High-resolution mass spectra (HRMS) were measured with a JEOL JMS-700 mass spectrometer by electron impact (EI), chemical ionization (CI), or fast atom bombardoment (FAB) method.

4.1.1. Materials

All chemicals were of reagent grade, and if necessary, were purified in the usual manner prior to use. Thin layer chromatography (TLC) was done with Merck 25 aluminium sheets (silica gel 60 F_{254}). Column chromatography was carried out with Wakogel C-200. All reactions were carried out under argon atmosphere.

4.2. General procedure for the intermolecular Pauson–Khand reaction

To a solution of *di*-cobalt octacarbonyl, $Co_2(CO)_8$ (103 mg, 0.30 mmol) in 1,2-dichloroethane (2.0 mL) was added fluorine-containing internal alkynes **2** (0.25 mmol) at r.t. After stirring for 2 h at r.t., the reaction mixture was cooled to 0 °C and 2-norbornene (71 mg, 0.75 mmol) was added to the solution. The whole was heated to the reflux temperature (*ca.* 84 °C) and stirred for 6 h at that temperature. Then the reaction mixture was again cooled to r.t., filtrated without quenching, and concentrated in *vacuo*. The residue was chromatographed on silica gel to afford the corresponding cyclopentenone derivatives **4** and **5**.

4.2.1. 3-(4-Chlorophenyl)-2-trifluoromethyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (*4a*)

Yield: 63%; ^1H NMR ($CDCl_3$) δ = 1.04 (d, *J* = 10.84 Hz, 1H), 1.12 (d, *J* = 10.84 Hz, 1H), 1.32–1.36 (m, 2H), 1.61–1.68 (m, 2H), 2.00 (br s, 1H), 2.47 (d, *J* = 5.54 Hz, 1H), 2.58 (br s, 1H), 3.05 (br d, *J* = 3.14 Hz, 1H), 7.28–7.31 (m, 2H), 7.42–7.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 28.33, 28.91, 31.47, 38.14, 39.69, 53.01, 54.30, 121.21 (q, *J* = 273.53 Hz), 128.66, 128.89, 132.19, 133.01 (q, *J* = 30.94 Hz), 136.72, 177.28 (q, *J* = 2.51 Hz), 203.15; ^{19}F NMR ($CDCl_3$) δ = −60.43 (s, 3F); IR (neat) 2962, 2916, 2878, 1717, 1639, 1593, 1491, 1456, 1400, 1366, 1308, 1269, 1236, 1188, 1167, 1130, 1094, 1067, 1014, 984, 937 cm^{-1}; HRMS (FAB^+) Calcd for (M+H) $C_{17}H_{15}ClF_3O$: 327.0764, Found 327.0768.

4.2.2. 2-(4-Chlorophenyl)-3-trifluoromethyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one

Yield: 29%; ^1H NMR ($CDCl_3$) δ = 1.15 (br s, 2H), 1.35–1.46 (m, 2H), 1.62–1.68 (m, 1H), 1.76–1.82 (m, 1H), 2.47 (d,

J = 3.35 Hz,1H), 2.56 (br s, 2H), 2.94 (d, J = 5.37 Hz, 1H), 7.18–7.21 (m, 2H), 7.37–7.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 28.22, 29.02, 31.30, 38.20, 40.15, 47.29, 53.62, 122.59 (q, J = 274.30 Hz), 127.41, 128.46, 130.22, 135.40, 147.61 (q, J = 3.27 Hz), 155.47 (q, J = 32.20 Hz), 207.33; ^{19}F NMR ($CDCl_3$) δ = −60.65 (s, 3F); IR (neat) 2962, 2930, 2876, 2856, 2360, 2343, 1720, 1595, 1493, 1458, 1400, 1366, 1304, 1246, 1232, 1177, 1159, 1132, 1113, 1094, 1016 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{17}H_{15}ClF_3O$: 327.0764, Found 327.0770.

4.2.3. 3-(4-Ethoxycarbonylphenyl)-2-trifluoromethyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (**4b**)

Yield: 66%; ^{1}H NMR ($CDCl_3$) δ = 1.00–1.09 (m, 1H), 1.14–1.18 (m, 1H), 1.28–1.40 (m, 2H), 1.41 (t, J = 7.19 Hz, 3H), 1.61–1.66 (m, 2H), 2.00 (br s, 1H), 2.49 (d, J = 5.20 Hz, 1H), 2.61 (br s, 1H), 3.05–3.08 (m, 1H), 4.41 (q, J = 7.19 Hz, 2H), 7.40 (d, J = 8.19 Hz, 2H), 8.13 (d, J = 8.19 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.39, 28.40, 28.99, 31.58, 38.01, 39.84, 53.34, 54.45, 61.47, 121.19 (q, J = 273.05 Hz), 127.14 (m), 129.75, 132.12, 133.67 (q, J = 31.12 Hz), 138.31, 165.81, 177.77 (q, J = 3.05 Hz), 203.29; ^{19}F NMR ($CDCl_3$) δ = −60.51 (s, 3F); IR (neat) 2962, 2876, 1719, 1644, 1608, 1406, 1365, 1276, 1188, 1130, 1020 cm^{-1}; HRMS (FAB$^+$) Calcd for (M$^+$) $C_{20}H_{19}F_3O_3$: 364.1286, Found 364.1288.

4.2.4. 2-(4-Ethoxycarbonylphenyl)-3-trifluoromethyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (**5b**)

Yield: 25%; ^{1}H NMR ($CDCl_3$) δ = 1.12–1.22 (m, 2H), 1.34–1.48 (m, 2H), 1.39 (t, J = 7.19 Hz, 3H), 1.60–1.70 (m, 1H), 1.74–1.84 (m, 1H), 2.49 (d, J = 5.60 Hz, 1H), 2.58 (br s, 2H), 2.97 (d, J = 5.99 Hz, 1H), 4.39 (q, J = 7.19 Hz, 2H), 7.31 (d, J = 7.99 Hz, 2H), 8.08 (d, J = 7.99 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.43, 28.34, 29.15, 31.47, 38.34, 40.29, 47.51, 53.86, 61.26, 122.63 (q, J = 274.13 Hz), 128.99 (m), 129.40, 131.13, 133.74, 148.18 (q, J = 3.31 Hz), 156.16 (q, J = 32.23 Hz), 166.21, 207.21; ^{19}F NMR ($CDCl_3$) δ = −60.64 (s, 3F); IR (neat) 2963, 2876, 1721, 1609, 1456, 1407, 1367, 1276, 1176, 1109, 1023 cm^{-1}; HRMS (FAB$^+$) Calcd for (M$^+$) $C_{20}H_{19}F_3O_3$: 364.1286, Found 364.1291.

4.2.5. 2-Trifluoromethyl-3-(4-methoxyphenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one

Yield: 64%; ^{1}H NMR ($CDCl_3$) δ = 0.99 (d, J = 10.75 Hz, 1H), 1.08 (d, J = 10.75 Hz, 1H), 1.35 (d, J = 11.22 Hz, 2H), 1.62 (d, J = 8.93 Hz, 2H), 1.99 (s, 1H), 2.44 (d, J = 5.56 Hz, 1H), 2.56 (s, 1H), 3.12 (d, J = 3.34 Hz, 1H), 3.86 (s, 3H), 6.99 (d, J = 8.71 Hz, 2H), 7.39 (d, J = 8.71 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 28.44, 28.89, 31.53, 38.70, 39.52, 52.41, 54.20, 55.36, 113.94, 121.65 (q, J = 273.55 Hz), 125.67, 129.80, 130.83 (q, J = 31.07 Hz), 161.77, 178.33 (q, J = 2.77 Hz), 203.57; ^{19}F NMR ($CDCl_3$) δ = −60.24 (s, 3F); IR (neat) 2961, 2876, 2843, 1713, 1605, 1572, 1514, 1458, 1421, 1367, 1298, 1261, 1238, 1180, 1115, 1067, 1030 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{18}H_{18}F_3O_2$: 323.1259, Found 323.1269.

4.2.6. 3-Trifluoromethyl-2-(4-methoxyphenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one

Yield: 26%; ^{1}H NMR ($CDCl_3$) δ = 1.10–1.18 (m, 2H), 1.34–1.44 (m, 2H), 1.59–1.68 (m, 1H), 1.75–1.80 (m, 1H), 2.44 (d, J = 5.39 Hz, 1H), 2.54 (br s, 2H), 2.92 (d, J = 5.42 Hz, 1H), 3.84 (s, 3H), 6.92–6.95 (m, 2H), 7.21–7.24 (m, 2H).

4.2.7. 2-Trifluoromethyl-3-(3-methoxyphenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one

Yield: 59%; ^{1}H NMR ($CDCl_3$) δ = 0.96 (d, J = 10.81 Hz, 1H), 1.07 (d, J = 10.81 Hz, 1H), 1.20–1.32 (m, 2H), 1.53–1.60 (m, 2H), 1.98 (br s, 1H), 2.38 (d, J = 5.50 Hz, 1H), 2.51 (br s, 1H), 2.98 (d, J = 3.12 Hz, 1H), 3.77 (s, 3H), 6.79 (br s, 1H), 6.85 (d, J = 7.99 Hz, 1H), 6.93 (dd, J = 7.99, 2.52 Hz, 1H), 7.30 (t, J = 7.99 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 28.34, 28.91, 31.47, 38.11, 39.68, 53.15, 54.26, 55.32, 112.99, 115.48, 119.45, 121.28 (q, J = 273.29 Hz), 129.63, 132.68 (q, J = 31.19 Hz), 135.15, 159.39, 178.85 (q, J = 2.77 Hz), 203.46; ^{19}F NMR ($CDCl_3$) δ = −60.40 (s, 3F); IR (neat) 2963, 2916, 2878, 1717, 1641, 1599, 1578, 1489, 1454, 1431, 1366, 1290, 1267, 1202, 1169, 1128, 1096, 1078, 1045 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{18}H_{18}F_3O_2$: 323.1259, Found 323.1254.

4.2.8. 3-Trifluoromethyl-2-(3-methoxyphenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one

Yield: 27%; ^{1}H NMR ($CDCl_3$) δ = 1.02–1.15 (m, 2H), 1.28–1.38 (m, 2H), 1.54–1.60 (m, 1H), 1.68–1.73 (m, 1H), 2.39 (d, J = 5.31 Hz, 1H), 2.49 (br s, 2H), 2.86 (d, J = 5.35 Hz, 1H), 3.73 (s, 3H), 6.70 (s, 1H), 6.75 (d, J = 8.01 Hz, 1H), 6.86 (d, J = 8.01, 2.43 Hz, 1H), 7.24 (t, J = 8.01 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ = −60.57 (s, 3F).

4.2.9. 2-Trifluoromethyl-3-(4-methoxybenzyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one

Yield: 57% (Combined yield); ^{1}H NMR ($CDCl_3$) δ = 1.02–1.08 (m, 2H), 1.20–1.26 (m, 2H), 1.55–1.69 (m, 2H), 2.21 (d, J = 5.53 Hz, 1H), 2.36 (d, J = 4.11 Hz, 1H), 2.49 (d, J = 3.74 Hz, 1H), 2.55 (d, J = 3.33 Hz, 1H), 3.61 (d, J = 14.46 Hz, 1H), 3.80 (s, 3H), 4.25 (d, J = 14.46 Hz, 1H), 6.86–6.89 (m, 2H), 7.10–7.12 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 28.20, 29.06, 31.56, 35.19, 38.08, 39.26, 50.47, 54.13, 55.25, 114.41, 121.94 (q, J = 273.42 Hz), 127.55, 129.95, 132.63 (q, J = 30.56 Hz), 158.80, 181.70 (q, J = 1.89 Hz), 203.87; ^{19}F NMR ($CDCl_3$) δ = −60.81 (s, 3F); IR (neat) 2959, 2876, 2839, 1717, 1639, 1611, 1512, 1456, 1421, 1364, 1303, 1252, 1126, 1036 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{19}H_{20}F_3O_2$: 337.1415, Found 337.1416.

4.2.10. 3-Ethoxycarbonyl-2-trifluoromethyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one

Yield: 69%; ^{1}H NMR ($CDCl_3$) δ = 1.11–1.16 (m, 2H), 1.29–1.38 (m, 2H), 1.35 (t, J = 7.14 Hz, 3H), 1.59–1.65 (m, 1H), 1.70–1.77 (m, 1H), 2.39 (d, J = 5.38 Hz, 1H), 2.46 (d, J = 4.26 Hz, 1H), 2.54 (d, J = 3.89 Hz, 1H), 2.95 (br d, J = 2.86 Hz, 1H), 4.37 (q, J = 7.14 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 13.91, 28.06, 28.76, 31.51, 37.85, 39.93, 49.75, 54.02, 62.55, 120.07 (q, J = 272.92 Hz), 134.28 (q, J = 32.95 Hz), 164.48, 167.05 (q, J = 3.14 Hz), 202.41; ^{19}F NMR ($CDCl_3$) δ = −63.22 (s, 3F); IR (neat) 3432, 2963, 2879, 1730, 1663, 1458, 1374, 1356, 1272, 1189, 1143, 1018, 988, 964, 943 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{14}H_{16}F_3O_3$: 289.1052, Found 289.1039.

4.2.11. 2-Difluoromethyl-3-(4-methoxyphenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (**4i**)

Yield: 24%; ^{1}H NMR ($CDCl_3$) δ = 0.98 (d, J = 10.79 Hz, 1H), 1.10 (d, J = 10.79 Hz, 1H), 1.30–1.50 (m, 2H), 1.60–1.80 (m, 2H), 2.01 (br s, 1H), 2.41 (d, J = 5.60 Hz, 1H), 2.53 (br s, 1H), 3.18 (br s, 1H), 3.87 (s, 3H), 6.48 (t, J = 54.52 Hz, 1H), 6.99 (d, J = 8.79 Hz, 2H), 7.60 (d, J = 8.79 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 28.83, 29.14, 31.77, 39.12, 39.39, 51.44, 54.17, 55.59, 110.88 (t, J = 235.14 Hz), 114.33, 125.59 (m), 130.92 (m), 133.25 (t, J = 21.94 Hz), 162.27, 176.55 (m), 206.75 (m); ^{19}F NMR ($CDCl_3$) δ = −123.71 (dd, J = 314.75, 54.52 Hz, 1F), −110.19 (dd, J = 314.75, 54.52 Hz, 1F); IR (neat) 2959, 2874, 2862, 1697, 1604, 1514, 1413, 1312, 1294, 1260, 1183, 1107, 1028 cm^{-1}; HRMS (FAB$^+$) Calcd for (M$^+$) $C_{18}H_{18}F_2O_2$: 304.1275, Found 304.1268.

4.2.12. 3-Difluoromethyl-2-(4-methoxyphenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (**5i**)

Yield: 53%; ^{1}H NMR ($CDCl_3$) δ = 1.00–1.20 (m, 2H), 1.30–1.48 (m, 2H), 1.56–1.68 (m, 1H), 1.70–1.80 (m, 1H), 2.40 (d, J = 5.60 Hz, 1H), 2.52 (m, 1H), 2.64 (br s, 1H), 2.96 (m, 1H), 3.83 (s, 3H), 6.47 (t, J = 54.85 Hz, 1H), 6.95 (d, J = 8.79 Hz, 2H), 7.26 (d, J = 8.79 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 28.53, 29.21, 31.52, 38.43, 40.03, 45.86 (m), 53.85, 55.43, 112.50 (t, J = 235.14 Hz),

114.22, 121.25, 130.57, 147.48 (t, J = 9.09 Hz), 158.50–159.10 (m), 160.50, 208.97; ^{19}F NMR ($CDCl_3$) δ = −119.73 (dd, J = 326.98, 54.85 Hz), −110.81 (dd, J = 326.98, 54.85 Hz); IR (neat) 2957, 2874, 2839, 1712, 1608, 1513, 1458, 1385, 1292, 1254, 1180, 1095, 1028 cm^{-1}; HRMS (FAB$^+$) Calcd for (M^+) $C_{18}H_{18}F_2O_2$: 304.1275, Found 304.1278.

*4.2.13. 2-Trifluoromethyl-3-(4-chlorophenyl)-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one (**4j**)*

Yield: 68% (Combined yield); ^{1}H NMR ($CDCl_3$) δ = 1.20–1.60 (m, 2H), 2.40–2.60 (m, 2H), 3.00–3.30 (m, 2H), 6.15–6.40 (m, 2H), 7.20–7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 41.69, 43.27, 44.44, 52.92, 53.36, 120.92 (q, J = 273.32 Hz), 128.69, 129.09, 132.09, 133.07 (q, J = 31.12 Hz), 136.98, 138.07, 138.29, 177.58, 201.87; ^{19}F NMR ($CDCl_3$) δ = −60.58 (s, 3F); IR (neat) 3080, 2989, 2951, 2882, 1710, 1615, 1592, 1492, 1362, 1327, 1308, 1196, 1058, 1014 cm^{-1}; HRMS (FAB$^+$) Calcd for (M^+) $C_{17}H_{12}ClF_3$: 324.0529, Found 324.0524.

*4.2.14. 3-Trifluoromethyl-2-(4-chlorophenyl)-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one (**5j**)*

^{19}F NMR ($CDCl_3$) δ = −61.41 (s, 3F).

4.3. Preparation of fluorine-containing propargyl alcohol **7**

To a solution of diisopropylamine (4.20 mL, 30 mmol) in THF (100 mL) was added 1.6 M n-BuLi solution in hexane (18.75 mL, 30 mmol) at −78 °C and the whole was stirred for 20 min. To this solution was added 2-bromo-3,3,3-trifluoropropene (1.50 mL, 15 mmol) very slowly. After stirring at −78 °C for 20 min, various aldehydes (10 mmol) or ketones (10 mmol) were added to the solution and the whole was stirred for 1 h at −78 °C. The reaction mixture was quenched with saturated NH_4Cl aq. and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was chromatographed on silica gel to afford fluorine-containing propargyl alcohols **7** and **8**.

*4.3.1. 1,1,1-Trifluoro-5,5-dimethyl-7-octen-2-yn-4-ol (**7a**)*

Yield: 73%; ^{1}H NMR ($CDCl_3$) δ = 1.00 (s, 3H), 1.02 (s, 3H), 2.04–2.22 (m, 3H), 4.18–4.22 (m, 1H), 5.10–5.13 (m, 2H), 5.78–5.87 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 22.46, 22.61, 38.72, 42.62, 69.38, 73.40 (q, J = 52.43 Hz), 86.94 (q, J = 21.88 Hz), 114.01 (q, J = 257.30 Hz), 118.55, 134.00; ^{19}F NMR ($CDCl_3$) δ = −56.76 (s, 3F); IR (neat) 3400, 2968, 2878, 2251, 1641, 1472, 1369, 1275, 1148, 1053, 1003, 920 cm^{-1}; HRMS (EI$^+$) Calcd for (M−H) $C_{10}H_{12}F_3O$: 205.0840, Found 205.0845.

*4.3.2. 1,1,1-Trifluoro-2-decyn-4-ol (**8a**)*

Yield: quant.; ^{1}H NMR ($CDCl_3$) δ = 0.89 (t, J = 6.94 Hz, 3H), 1.25–1.36 (m, 6H), 1.40–1.48 (m, 2H), 1.71–1.81 (m, 2H), 2.84 (br s, 1H), 4.45 (ddq, J = 3.29, 3.29, 3.29 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.90, 22.50, 24.76, 28.72, 31.58, 36.65, 61.79, 72.02 (q, J = 52.85 Hz), 87.91 (q, J = 6.18 Hz), 114.07 (q, J = 257.45 Hz); ^{19}F NMR ($CDCl_3$) δ = −50.94 (s, 3F); IR (neat) 3330, 2933, 2862, 2271, 1468, 1381, 1275, 1220, 1144, 1046 cm^{-1}.

*4.3.3. 6,6,6-Trifluoro-1-phenyl-4-hexyn-3-ol (**8b**)*

Yield: 80%; ^{1}H NMR ($CDCl_3$) δ = 2.11–2.23 (m, 2H), 2.89 (t, J = 7.72 Hz, 2H), 3.35 (br s, 1H), 4.48 (br s, 1H), 7.29–7.35 (m, 3H), 7.40–7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 30.88, 37.87, 60.72, 72.20 (q, J = 52.95 Hz), 87.64 (q, J = 6.36 Hz), 114.05 (q, J = 257.33 Hz), 126.29, 128.38, 128.56, 140.21; ^{19}F NMR ($CDCl_3$) δ = −50.78 (s, 3F); IR (neat) 3366, 3088, 3066, 3030, 2956, 2931, 2866, 2269, 1710, 1604, 1497, 1455, 1379, 1275, 1140, 1049, 1017, 915 cm^{-1}; HRMS (FAB$^+$) Calcd for (M^+) $C_{12}H_{11}F_3O$: 228.0762, Found 228.0765.

*4.3.4. 1-Cyclohexyl-4,4,4-trifluoro-2-butyn-1-ol (**8c**)*

Yield: quant.; ^{1}H NMR ($CDCl_3$) δ = 1.01–1.34 (m, 6H), 1.58–1.66 (m, 1H), 1.66–1.72 (m, 4H), 3.22 (br s, 1H), 4.23 (ddq, J = 3.08, 3.18, 3.08 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 25.58, 25.60, 26.07, 27.92, 28.32, 43.40, 66.46, 72.77 (q, J = 52.80 Hz), 87.21 (q, J = 6.31 Hz), 114.06 (q, J = 257.07 Hz); ^{19}F NMR ($CDCl_3$) δ = −50.73 (s, 3F); IR (neat) 3612, 3334, 2926, 2857, 2674, 2275, 1452, 1402, 1278, 1140, 1085, 1038, 999 cm^{-1}; MS (EI$^+$) m/z (rel. intensity) 123 (M-C_6H_{11}, 89.40), 83 (M-$C_4H_2F_3O$, 100.0), 58 (100.0).

*4.3.5. 5-Ethyl-1,1,1-trifluoro-2-heptyn-4-ol (**8d**)*

Yield: 99%; ^{1}H NMR ($CDCl_3$) δ = 0.93 (t, J = 7.37 Hz, 3H), 0.94 (t, J = 7.41 Hz, 3H), 1.35–1.43 (m, 1H), 1.45–1.53 (m, 3H), 1.54–1.62 (m, 1H), 2.87 (br s, 1H), 4.49 (ddq, J = 5.05, 5.05, 2.48 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 11.07, 11.22, 21.59, 21.72, 46.79, 64.07, 72.77 (q, J = 52.63 Hz), 87.42 (q, J = 6.40 Hz), 114.07 (q, J = 257.45 Hz); ^{19}F NMR ($CDCl_3$) δ = −50.82 (s, 3F); IR (neat) 3614, 3346, 2969, 2882, 2744, 2548, 2424, 2257, 1713, 1611, 1464, 1385, 1275, 1140, 1028, 941 cm^{-1}; HRMS (EI$^+$) Calcd for (M^+) $C_9H_{13}F_3O$: 194.0918, Found 194.0914.

*4.3.6. 1-Trifluoropropynylcyclohexanol (**8e**)*

Yield: 96%; ^{1}H NMR ($CDCl_3$) δ = 1.23–1.32 (m, 1H), 1.47–1.59 (m, 3H), 1.60–1.67 (m, 2H), 1.70–1.77 (m, 2H), 1.92–1.98 (m, 2H), 2.33 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 22.71, 24.73, 38.85, 68.35, 71.56 (q, J = 52.58 Hz), 90.62 (q, J = 6.28 Hz), 114.19 (q, J = 257.20 Hz); ^{19}F NMR ($CDCl_3$) δ = −50.58 (s, 3F); IR (KBr) 3251, 2948, 2868, 2280, 2250, 1454, 1347, 1298, 1267, 1218, 1141, 1076, 1033, 969 cm^{-1}; HRMS (EI$^+$) Calcd for (M−H) $C_9H_{10}F_3O$: 191.0684, Found 191.0669.

4.4. Preparation of difluoromethyl-containing propargyl alcohol

To a solution of 2,3,3-trifluoro-1-iodopropene (3.3 g, 15 mmol) in THF (100 mL) was added 1.6 M n-BuLi hexane solution (18.75 mL, 30 mmol) at −78 °C. After stirring for 1 h, n-heptanal (1.39 mL, 10 mmol) was added to the solution at −78 °C and the whole was stirred for 1 h. The reaction mixture was quenched with saturated NH_4Cl aq. and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was chromatographed on silica gel to afford fluorine-containing propargyl alcohol **8f**.

*4.4.1. 1,1-Difluoro-2-decyn-4-ol (**8f**)*

Yield: 98%; ^{1}H NMR ($CDCl_3$) δ = 0.87 (t, J = 7.00 Hz, 3H), 1.24–1.34 (m, 6H), 1.39–1.45 (m, 2H), 1.67–1.78 (m, 2H), 3.20 (br s, 1H), 4.42 (ddt, J = 4.87, 4.87, 6.02 Hz, 1H), 6.19 (td, J = 55.42, 0.76 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.91, 22.48, 24.83, 28.76, 31.59, 36.88, 61.85, 75.79 (t, J = 33.98 Hz), 89.88 (t, J = 7.29 Hz), 103.60 (t, J = 232.05 Hz); ^{19}F NMR ($CDCl_3$) δ = −106.38 (dd, J = 55.42, 4.89 Hz, 2F); IR (neat) 3603, 3354, 2929, 2861, 2314, 2253, 1713, 1467, 1372, 1340, 1156, 1121, 1047 cm^{-1}; HRMS (EI$^+$) Calcd for (M−H) $C_{10}H_{15}F_2O$: 189.1091, Found 189.1085.

4.5. Preparation of fluorine-containing propargyl acetate (**7b**)

To a solution of **7a** (1.03 g, 5.0 mmol) in CH_2Cl_2 (25 mL) was added pyridine (0.81 mL, 10 mmol) and acetic anhydride (0.95 mL, 10 mmol) at 0 °C and the whole was stirred for 12 h at r.t. The reaction mixture was quenched with saturated NH_4Cl aq. and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was chromatographed on silica gel to afford fluorine-containing acetate **7b** (1.10 g, 4.45 mmol).

*4.5.1. 2,2-Dimethyl-1-trifluoropropynyl-4-pentenyl acetate (**7b**)*

Yield: 89%; ^{1}H NMR ($CDCl_3$) δ = 1.02 (s, 3H), 1.03 (s, 3H), 2.13 (s, 5H), 4.95–5.15 (m, 2H), 5.21 (q, *J* = 2.91 Hz, 1H), 5.72–5.81 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 20.57, 22.57, 22.85, 37.87, 42.73, 69.05, 73.16 (q, *J* = 52.68 Hz), 83.61 (q, *J* = 6.43 Hz), 113.82 (q, *J* = 257.81 Hz), 118.82, 133.05, 169.51; ^{19}F NMR ($CDCl_3$) δ = −50.98 (s, 3F); IR (neat) 2974, 2935, 2882, 2438, 2266, 1751, 1716, 1641, 1421, 1364, 1283, 1229, 1150, 1092, 1022, 906 cm^{-1}.

*4.6. Preparation of fluorine-containing propargyl silyl ether (**7c**)*

To a solution of imidazole (511 mg, 7.50 mmol) and *t*-butyldimethylsilyl chloride, TBSCl (453 mg, 3.00 mmol) in DMF (7.50 mL) was added **7a** (309 mg, 1.50 mmol) at r.t. and the whole was stirred for 10 h at 70 °C. The reaction mixture was quenched with saturated NH_4Cl aq. and extracted with diethyl ether three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was chromatographed on silica gel to afford fluorine-containing acetate **7c** (333 mg, 1.04 mmol).

*4.6.1. 4-(tert-Butyldimethylsilyloxy)-1,1,1-trifluoro-5,5-dimethyl-7-octen-2-yne (**7c**)*

Yield: 69%; ^{1}H NMR ($CDCl_3$) δ = 0.10 (s, 3H), 0.15 (s, 3H), 0.92 (s, 9H), 0.94 (s, 3H), 0.96 (s, 3H), 2.00–2.20 (m, 2H), 4.10 (q, *J* = 3.06 Hz, 1H), 5.00–5.15 (m, 2H), 5.70–5.90 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = −5.34, −4.68, −2.96, 18.10, 22.40, 22.55, 25,62, 25.69, 39.23, 42.40, 69.86, 73.00 (q, *J* = 52.30 Hz), 88.07 (q, *J* = 6.41 Hz), 114.10 (q, *J* = 257.43 Hz), 117.99, 134.18; ^{19}F NMR ($CDCl_3$) δ = −50.85 (s, 3F); IR (neat) 2960, 2932, 2860, 2251, 2141, 1717, 1420, 1364, 1277, 1221, 1146, 1094, 1007, 901 cm^{-1}; MS (EI^+) *m*/*z* (rel. intensity) 263 (M−C_4H_9, 100.0).

*4.7. Preparation of fluorine-containing allyl propargyl ether **9***

To a solution of NaH (36 mg, 0.75 mmol) in THF (1.25 mL) was added dimethylpropylene urea (DMPU) (0.24 mL, 2.00 mmol), **8** (0.50 mmol), and allyl bromide (0.17 mL, 2.00 mmol) at−78 °C. The whole was stirred for 5 min. at −78 °C followed by warming up to r.t. After stirring for 20 min at r.t., the reaction mixture was quenched with saturated NH_4Cl aq. and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was chromatographed on silica gel to afford fluorine-containing allyl propargyl ether **9**.

*4.7.1. 4-Allyloxy-1,1,1-trifluoro-2-decyne (**9a**)*

Yield: 85%; ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, *J* = 6.99 Hz, 3H), 1.25–1.34 (m, 6H), 1.40–1.47 (m, 2H), 1.71–1.82 (m, 2H), 3.96 (dd, *J* = 12.53 Hz, 6.37 Hz, 1H), 4.15 (ddq, *J* = 6.57, 6.57, 3.13 Hz, 1H), 4.22 (ddt, *J* = 12.52, 5.11, 1.30 Hz, 1H), 5.23 (dd, *J* = 10.38, 1.21 Hz, 1H), 5.31 (ddt, *J* = 17.21, 1.51, 1.38 Hz, 1H), 5.85–5.93 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.94, 22.51, 24.91, 28.81, 31.59, 34.76, 68.03, 70.31, 72.78 (q, *J* = 52.42 Hz), 86.76 (q, *J* = 6.41 Hz), 114.02 (q, *J* = 257.07 Hz), 118.07, 133.60; ^{19}F NMR ($CDCl_3$) δ = −50.68 (s, 3F); IR (neat) 3086, 2931, 2861, 2268, 1736, 1649, 1460, 1423, 1379, 1337, 1276, 1147, 1091, 995 cm^{-1}; HRMS (FAB^+) Calcd for (M−H) $C_{13}H_{18}F_3O$: 247.1310, Found 247.1299.

*4.7.2. 4-Allyloxy-1,1,1-trifluoro-6-phenyl-2-hexyne (**9b**)*

Yield: 67%; ^{1}H NMR ($CDCl_3$) δ = 2.13–2.20 (m, 1H), 2.22–2.29 (m, 1H), 2.90 (t, *J* = 7.60 Hz, 2H), 4.04 (dddt, *J* = 12.48, 6.28, 1.21, 1.21 Hz, 1H), 4.19–4.23 (m, 1H), 4.34 (dddt, *J* = 12.43, 5.16, 1.38, 1.43 Hz, 1H), 5.34 (dt, *J* = 10.38, 1.13 Hz, 1H), 5.44 (dt, *J* = 17.18, 1.49 Hz, 1H), 5.98–6.05 (m, 1H), 7.28–7.33 (m, 3H), 7.38–7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 31.04, 36.30, 67.06, 70.39, 73.08 (q, *J* = 52.41 Hz), 86.47 (q, *J* = 6.28 Hz), 114.02 (q, *J* = 257.33 Hz), 118.07, 126.22, 128.46, 128.52, 133.51, 140.49; ^{19}F NMR ($CDCl_3$) δ = −50.66 (s, 3F); IR (neat) 3030, 2930, 2866, 2264, 1497, 1456, 1427, 1277, 1144, 1096, 1061, 995, 932 cm^{-1}; HRMS (EI^+) Calcd for (M^+) $C_{15}H_{15}F_3O$: 268.1075, Found 268.1062.

*4.7.3. 1-Allyloxy-1-cyclohexyl-4,4,4-trifluoro-2-butyne (**9c**)*

Yield: 91%; ^{1}H NMR ($CDCl_3$) δ = 1.04–1.30 (m, 5H), 1.66–1.87 (m, 6H), 3.91–3.96 (m, 2H), 4.23 (ddt, *J* = 12.64, 5.03, 1.44 Hz, 1H), 5.21 (ddt, *J* = 10.40, 1.38, 1.19 Hz, 1H), 5.31 (ddt, *J* = 17.24, 1.57, 1.54 Hz, 1H), 5.84–5.91 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 25.70, 25.74, 26.19, 28.31, 28.68, 42.14, 70.45, 72.89, 73.56 (q, *J* = 52.31 Hz), 86.10 (q, *J* = 6.35 Hz), 114.05 (q, *J* = 257.33 Hz), 117.89, 133.69; ^{19}F NMR ($CDCl_3$) δ = −50.51 (s, 3F); IR (neat) 3437, 3085, 3018, 2926, 2857, 2666, 2254, 1736, 1649, 1453, 1424, 1411, 1374, 1332, 1279, 1215, 1140, 998 cm^{-1}.

*4.7.4. 4-Allyloxy-5-ethyl-1,1,1-trifluoro-2-heptyne (**9d**)*

Yield: 98%; ^{1}H NMR ($CDCl_3$) δ = 0.91 (t, *J* = 7.40 Hz, 3H), 0.92 (t, *J* = 7.41 Hz, 3H), 1.35–1.42 (m, 1H), 1.46–1.51 (m, 2H), 1.56–1.64 (m, 2H), 3.94 (ddt, *J* = 12.66, 6.41, 1.27 Hz, 1H), 4.17 (ddq, *J* = 2.91, 2.21, 2.91 Hz, 1H), 4.24 (ddt, *J* = 12.64, 4.99, 1.57 Hz, 1H), 5.23 (ddt, *J* = 10.40, 1.29, 1.38 Hz, 1H), 5.32 (ddt, *J* = 17.23, 1.57, 1.57 Hz, 1H), 5.85–5.93 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 11.32, 11.41, 21.99, 22.06, 45.58, 70.50, 70.59, 73.55 (q, *J* = 52.53 Hz), 86,36 (q, *J* = 6.38 Hz), 114.02 (q, *J* = 256.95 Hz), 117.93, 133.72; ^{19}F NMR ($CDCl_3$) δ = −50.54 (s, 3F); IR (neat) 3086, 2967, 2939, 2880, 2261, 1736, 1649, 1463, 1424, 1412, 1383, 1330, 1275, 1215, 1143, 1078, 998 cm^{-1}; HRMS (FAB^+) Calcd for (M-H) $C_{12}H_{16}F_3O$: 233.1153, Found 233.1160.

*4.7.5. 1-Allyloxy-1-trifluoropropynylcyclohexane (**9e**)*

Yield: 51%; ^{1}H NMR ($CDCl_3$) δ = 1.35–2.05 (m, 10H), 4.09 (dt, *J* = 5.46, 1.14 Hz, 2H), 5.15–5.21 (m, 1H), 5.31 (dd, *J* = 17.20, 1.60 Hz, 1H), 5.90–5.98 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 22.31, 25.04, 36.26, 64.96, 73.14 (q, *J* = 52.51 Hz), 73.21, 89.00 (q, *J* = 6.34 Hz), 114.18 (q, *J* = 256.95 Hz), 116.64, 134.64; ^{19}F NMR ($CDCl_3$) δ = −50.35 (s, 3F); IR (neat) 3084, 2940, 2864, 2270, 1729, 1693, 1681, 1648, 1451, 1426, 1385, 1353, 1264, 1140, 1030, 995 cm^{-1}.

*4.7.6. 4-Allyloxy-1,1-difluoro-2-decyne (**9f**)*

Yield: 56%; ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, *J* = 6.92 Hz, 3H), 1.25–1.33 (m, 6H), 1.40–1.47 (m, 2H), 1.69–1.81 (m, 2H), 3.95 (dd, *J* = 12.53, 6.32 Hz, 1H), 4.14 (tdd, *J* = 5.97, 4.95, 4.95 Hz, 1H), 4.22 (dd, *J* = 12.56, 5.09 Hz, 1H), 5.20 (d, *J* = 10.39 Hz, 1H), 5.30 (dd, *J* = 17.23, 1.36 Hz, 1H), 5.85–5.92 (m, 1H), 6.21 (t, *J* = 55.42 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.94, 22.50, 24.97, 28.83, 31.59, 34.99, 68.27 (t, *J* = 1.67 Hz), 70.01, 76.75 (t, *J* = 33.71 Hz), 88.31 (t, *J* = 7.19 Hz), 103.55 (t, *J* = 232.05 Hz), 117.76, 133.83; ^{19}F NMR ($CDCl_3$) δ = –106.15 (dd, *J* = 55.42, 4.51 Hz, 2F); IR (neat) 3435, 3084, 2930, 2861, 2251, 1732, 1648, 1460, 1426, 1410, 1373, 1336, 1272, 1155, 1047, 931 cm^{-1}; HRMS (FAB^+) Calcd for (M−H) $C_{13}H_{19}F_2O$: 229.1404, Found 229.1413.

4.8. General procedure for the intramolecular Pauson–Khand reaction

To a solution of $Co_2(CO)_8$ (68 mg, 0.20 mmol) in THF (2.00 mL) was added fluorine-containing enynes **7a–c** or allyl propargyl ethers **9** (0.20 mmol) at r.t. After stirring for 1 h at r.t. the reaction mixture was cooled to 0 °C. To the solution was added *N*-methylmorpholine *N*-oxide, NMO (1.5, 3.0, or 6.0 equiv.) or trimethylamine *N*-oxide dihydrate, TMANO·$2H_2O$ (1.5, 3.0, or 6.0 equiv.) at 0 °C. Then the whole was stirred for 1 h at r.t. The reaction mixture was quenched with saturated NH_4Cl aq. and NaCl aq. and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and

concentrated in *vacuo*. The residue was chromatographed on silica gel to afford cyclopentenone derivatives **11a–c**, **12a–e**.

*4.8.1. 3-Trifluoromethyl-4-hydroxy-5,5-dimethyl-4,5,6,6a-tetrahydro-2(1H)-pentalenone (**11a**)*

Yield: 67%.

Major isomer

^{1}H NMR ($CDCl_3$) δ = 1.08 (s, 3H), 1.20 (s, 3H), 1.46 (dd, J = 12.51, 11.09 Hz, 1H), 1.97–2.04 (m, 1H), 2.24 (br s, 1H), 2.24 (dd, J = 17.97, 3.82 Hz, 1H), 2.78 (d, J = 17.96, 6.80 Hz, 1H), 3.10–3.16 (m, 1H), 4.61 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 23.61, 28.25, 39.98, 42.75, 43.43, 44.87, 75.51, 121.26 (q, J = 271.64 Hz), 127.88 (q, J = 33.58 Hz), 192.50 (q, J = 2.52 Hz), 201.95; ^{19}F NMR ($CDCl_3$) δ = −60.99 (s, 3F); IR (neat) 3447, 2962, 2936, 2872, 1716, 1672, 1360, 1132, 1065, 1011, 941 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{11}H_{14}F_3O_2$: 235.0946, Found 235.0937.

Minor isomer

^{1}H NMR ($CDCl_3$) δ = 1.05 (s, 3H), 1.19 (s, 3H), 1.25 (dd, J = 8.49, 7.14 Hz, 1H), 1.97–2.04 (m, 1H), 2.11 (dd, J = 12.80, 9.70 Hz, 1H), 2.23 (br s, 1H), 2.79–2.84 (m, 1H), 3.42–3.47 (m, 1H), 4.51 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 22.36, 28.75, 40.94, 42.54, 43.88, 44.55, 75.51, 121.28 (q, J = 272.02 Hz), 127.62 (q, J = 33.20 Hz), 188.63, 202.55; ^{19}F NMR ($CDCl_3$) δ = −62.54 (s, 3F); IR (neat) 3447, 2962, 2936, 2872, 1716, 1672, 1360, 1132, 1065, 1011, 941 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{11}H_{14}F_3O_2$: 235.0946, Found 235.0937.

*4.8.2. 4-(Acetyloxy)-3-trifluoromethyl-5,5-dimethyl-4,5,6,6a-tetrahydro-2(1H)-pentalenone (**11b**)*

Yield: 52%.

Major isomer

^{1}H NMR ($CDCl_3$) δ = 1.11 (s, 3H), 1.15 (s, 3H), 1.24 (dd, J = 12.77, 10.47 Hz, 1H), 2.12 (s, 3H), 2.12–2.15 (m, 1H), 2.24 (dd, J = 18.25, 3.48 Hz, 1H), 2.80 (t, J = 7.21 Hz, 1H), 3.35–3.41 (m, 1H), 5.68 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 20.42, 23.12, 28.78, 41.23, 43.22, 44.06, 44.62, 75.60, 120.74 (q, J = 271.39 Hz), 128.44 (q, J = 23.01 Hz), 169.47, 184.23 (q, J = 3.27 Hz), 201.88; ^{19}F NMR ($CDCl_3$) δ = −63.10 (s, 3F); IR (neat) 2968, 2939, 2874, 1732, 1684, 1373, 1317, 1236, 1196, 1134, 1045, 941, 912 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{13}H_{16}F_3O_3$: 277.1052, Found 277.1054.

Minor isomer

^{1}H NMR ($CDCl_3$) δ = 1.02 (s, 3H), 1.28 (s, 3H), 1.43 (t, J = 12.23 Hz, 1H), 2.02 (dd, J = 12.43, 8.11 Hz, 1H), 2.12 (s, 3H), 2.28 (dd, J = 18.18, 3.46 Hz, 1H), 2.84 (t, J = 6.78 Hz, 1H), 3.19–3.24 (m, 1H), 5.82 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 20.21, 23.56, 27.99, 40.77, 42.82, 43.50, 44.72, 76.21, 120.75 (q, J = 272.65 Hz), 128.71 (q, J = 23.14 Hz), 169.79, 188.45 (q, J = 2.52 Hz), 201.19; ^{19}F NMR ($CDCl_3$) δ = −62.11 (s, 3F); IR (neat) 2968, 2939, 2874, 1732, 1684, 1373, 1317, 1236, 1196, 1134, 1045, 941, 912 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{13}H_{16}F_3O_3$: 277.1052, Found 277.1054.

*4.8.3. 4-(tert-Butyldimethylsilyloxy)-3-trifluoromethyl-5,5-dimethyl-4,5,6,6a-tetrahydro-2(1H)-pentalenone (**11c**)*

Yield: 53%.

Major isomer

^{1}H NMR ($CDCl_3$) δ = 0.02 (s, 3H), 0.12 (s, 3H), 0.84 (s, 3H), 0.88 (s, 9H), 1.16 (s, 3H), 1.16 (dd, J = 13.03, 6.32 Hz, 1H), 2.04–2.20 (m, 2H), 2.85 (dd, J = 18.29, 7.07 Hz, 1H), 3.43–3.49 (m, 1H), 4.35 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 0.99, 14.09, 18.08, 22.63, 23.77, 25.62, 28.33, 31.57, 39.80, 41.62, 44.87, 45.13, 76.06, 121.16 (q, J = 272.02 Hz), 125.74 (q, J = 32.95 Hz), 189.22 (q, J = 2.89 Hz), 203.12; ^{19}F NMR ($CDCl_3$) δ = −62.54 (s, 3F); IR (neat) 2957, 2932, 2860, 1732, 1684, 1472, 1362, 1344, 1261, 1230, 1215, 1140, 1094, 939 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{17}H_{28}F_3O_2{}^{28}Si$: 349.1811, Found 349.1802.

Minor isomer

^{1}H NMR ($CDCl_3$) δ = 0.07 (s, 3H), 0.12 (s, 3H), 0.89 (s, 3H), 0.94 (s, 9H), 1.19 (s, 3H), 1.40 (dd, J = 13.50, 7.75 Hz, 1H), 2.04–2.15 (m, 2H), 2.76 (dd, J = 18.09, 7.25 Hz, 1H), 3.00–3.06 (m, 1H), 4.72 (d, J = 1.66 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = –3.96, 14.10, 18.07, 22.64, 24.22, 25.93, 28.71, 31.57, 35.89, 42.25, 44.07, 44.41, 80.18, 121.04 (q, J = 272.65 Hz), 126.82 (q, J = 34.21 Hz), 190.55 (q, J = 2.64 Hz), 202.27; ^{19}F NMR ($CDCl_3$) δ = −58.45 (s, 3F); IR (neat) 2957, 2932, 2860, 1732, 1684, 1472, 1362, 1344, 1261, 1230, 1215, 1140, 1094, 939 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{17}H_{28}F_3O_2{}^{28}Si$: 349.1811, Found 349.1818.

*4.8.4. 1-Hexyl-6-trifluoromethyl-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (**12a**)*

Yield: 34%; ^{1}H NMR ($CDCl_3$) δ = 0.87 (t, J = 6.86 Hz, 3H), 1.24–1.48 (m, 8H), 1.68–1.83 (m, 2H), 2.28 (dd, J = 18.10, 2.92 Hz, 1H), 2.71–2.78 (m, 1H), 3.31–3.39 (m, 2H), 4.36–4.43 (m, 1H), 4.83 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.96, 22.48, 25.17, 28.90, 31.54, 33.72, 39.52, 44.00, 70.61, 76.38, 121.05 (q, J = 271.41 Hz), 125.95 (q, J = 34.34 Hz), 188.43, 200.97; ^{19}F NMR ($CDCl_3$) δ = −62.33 (s, 3F); IR (neat) 2955, 2929, 2859, 1734, 1687, 1468, 1370, 1342, 1310, 1205, 1137, 1023, 951, 929 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{14}H_{20}F_3O_2$: 277.1415, Found 277.1414; Anal. Calcd for $C_{14}H_{19}F_3O_2$: C, 60.86; H, 6.93. Found: C, 61.20; H, 6.57.

*4.8.5. 6-Trifluoromethyl-1-(2-phenylethyl)-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (**12b**)*

Yield: 45%; ^{1}H NMR ($CDCl_3$) δ = 1.99–2.06 (m, 1H), 2.12–2.19 (m, 1H), 2.29 (dd, J = 18.12, 2.90 Hz, 1H), 2.74–2.84 (m, 3H), 3.34–3.41 (m, 2H), 4.44 (br s, 1H), 4.82 (br d, J = 8.27 Hz, 1H), 7.20–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 31.35, 35.18, 39.55, 44.04, 70.70, 75.52, 120.98 (q, J = 271.39 Hz), 126.06 (q, J = 34.46 Hz), 126.24, 128.41, 128.50, 140.47, 188.04 (q, J = 3.14 Hz), 200.77; ^{19}F NMR ($CDCl_3$) δ = −62.32 (s, 3F); IR (neat) 3028, 2862, 1732, 1690, 1497, 1456, 1371, 1344, 1310, 1132, 1030, 991, 949, 928, 912 cm^{-1}; HRMS (FAB$^+$) Calcd for (M+H) $C_{16}H_{16}F_3O_2$: 297.1102, Found 297.1103.

*4.8.6. 1-Cyclohexyl-6-trifluoromethyl-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (**12c**)*

Yield: 35%; ^{1}H NMR ($CDCl_3$) δ = 1.12–1.32 (m, 5H), 1.58–1.62 (m, 1H), 1.65–1.70 (m, 2H), 1.73–1.80 (m, 3H), 2.27 (dd, J = 17.85, 2.87 Hz, 1H), 2.72–2.78 (m, 1H), 3.28–3.35 (m, 2H), 4.35–4.41 (m, 1H), 4.68 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ = 25.91, 26.20, 27.83, 29.31, 39.60, 41.97, 44.23, 70.35, 80.76, 121.01 (q, J = 271.79 Hz), 126.83 (q, J = 33.96 Hz), 187.42 (q, J = 3.14 Hz), 201.23; ^{19}F NMR ($CDCl_3$) δ = −62.20 (s, 3F); HRMS (FAB$^+$) Calcd for (M+H) $C_{14}H_{18}F_3O_2$: 275.1259, Found 275.1269; Anal. Calcd for $C_{14}H_{17}F_3O_2$: C, 61.31; H, 6.25. Found: C, 61.07; H, 6.15.

*4.8.7. 1-(1-Ethylpropyl)-6-trifluoromethyl-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (**12d**)*

Yield: 51%; ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, J = 7.49 Hz, 3H), 0.97 (t, J = 7.44 Hz, 3H), 1.28–1.34 (m, 1H), 1.38–1.45 (m, 2H), 1.50–1.57

(m, 1H), 1.67–1.72 (m, 1H), 2.28 (ddd, J = 18.00, 2.89, 0.70 Hz, 1H), 2.72–2.78 (m, 1H), 3.28–3.34 (m, 2H), 4.34–4.40 (m, 1H), 4.88 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ = 11.55, 22.05, 22.55, 39.76, 44.71, 44.96, 70.22, 78.37, 121.10 (q, J = 271.54 Hz), 126.29 (q, J = 33.83 Hz), 189.40 (q, J = 2.77 Hz), 201.05; ^{19}F NMR ($CDCl_3$) δ = −62.14 (s, 3F); IR (neat) 2966, 2937, 2878, 1732, 1682, 1463, 1412, 1368, 1339, 1306, 1286, 1233, 1205, 1136, 1049, 1023, 1000, 953 cm^{-1}; HRMS (EI$^+$) Calcd for $C_{13}H_{17}F_3O_2$: 262.1181, Found 262.1192.

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